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(54) Lithium aluminoborate glass-ceramics

(57) This invention is directed to the production of thermally crystallizable glasses which, upon heat treatment in contact with alumina particulates, will form a strong glass-ceramic-bonded composite body, the excellent bonding being attributed to the presence of lithium aluminoborate crystals. The glass-ceramic composition consists essentially, in weight percent, of

SiO_2	25-55	MgO	0-12
B_2O_3	35-65	Li_2O+MgO	4-16 .
Li_2O	2-15		

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Description

This invention is related to the production of glass-ceramic materials having compositions especially well suited for bonding particulate ceramic materials into dense, strong composite articles.

The fabrication of composite articles comprising particulate ceramic materials bonded with a glass-ceramic has been practiced for a number of years. Examples are illustrated in U. S. Patents No. 4,861,734, 5,112,777, and 5,256,603.

The Patent No. 5,112,777 describes a field of divalent metal borate and borosilicate glass compositions that yield unusually strong glass-ceramic bonds when combined with Al_2O_3 and/or other ceramic phases in particulate form and fired. The crystalline phases, consisting principally of borate and/or alumina borates, can develop as a direct result of reaction/dissolution of borate or borosilicate glasses with refractory ceramic phases, most commonly Al_2O_3.

Our laboratory investigations have discovered a new family of thermally crystallizable lithium borosilicate glasses which can react with particulate Al_2O_3 in a different fashion from that described in Patent No. 5,256,603, supra, to form an exceptionally strong glass-ceramic bond with the particulate Al_2O_3, as measured in flexural and compression tests performed on fired composite articles. The preferred composite articles are comprised of about 10-30% by weight lithium borosilicate glass powder and about 70-90% by weight of alumina particles. The materials are mixed together, shaped into an article of a desired configuration, and then fired at temperatures between about 750°-950°, preferably 850°-900°C, for a period of time sufficient to cause the particles to react together to form a sintered glass-ceramic-bonded ceramic composite comprising Al_2O_3 particulates bonded together by a glass-ceramic.

The bonding glass-ceramic comprises an interlocking, cross-bladed network of lath-like lithium aluminoborate crystals developed through interaction of the lithium borosilicate glass with the particulate Al_2O_3 during the sintering firing. Because of the very high strengths exhibited by these glass-ceramic bonds, they can provide a significant improvement in the performance of bonded alumina composites for applications such as abrasives, coatings, and electronic substrates. The inventive bonded composites demonstrate properties that can make them competitive in the abrasive field with the much more expensive super abrasives.

The precursor glasses to be fired into the desired glass-ceramic bonds consist essentially, expressed in terms of weight percent on the oxide basis, of about

SiO_2	25-55	MgO	0-12
B_2O_3	35-65	Li_2O+MgO	4-16
Li_2O	2-15		

The expression "consist essentially of" is intended to allow the inclusion of minor portions of inorganic oxide components that are not detrimental to the desired properties of the inventive glass-ceramic and, most vitally, do not adversely affect the bond developed through the interaction of the lithium borosilicate glass with the particulate alumina.

The above-cited composition intervals have been found to be critical in producing glasses exhibiting the demanded properties. To illustrate:

At least 25% SiO_2 is required to assure good glass flow and wetting of the alumina particles, and to inhibit essentially instantaneous crystallization when the precursor glass is subjected to the crystallization heat treatment. That is, the glass must flow sufficiently to wet and react with the alumina particles to form the desired bond. The presence of SiO_2 also enhances the chemical durability of the glass. Where the level of SiO_2 exceeds 55%, however, the glass becomes quite refractory and flow thereof is reduced. Furthermore, high levels of SiO_2 can render the glass prone to phase separation.

A concentration of B_2O_3 of at least 35% is required to assure good flow of the glass. That is, B_2O_3 levels less than 35% result in glass exhibiting relatively high refractoriness with consequent less flow. On the other hand, concentrations of B_2O_3 above 65% lead to decreased chemical durability in the glass and unwanted crystallization, e.g., $9Al_2O_3 \cdot 2B_2O_3$ crystals may occur.

The presence of at least 2% Li_2O assures good glass flow and the formation of the lithium aluminoborate crystal phase, that phase believed to have the formula $2Li_2O \cdot 3Al_2O_3 \cdot 2B_2O_3$, but its adverse effect upon the overall cost of the bond is one basis for limiting its use to 15%. Furthermore, the reaction of high Li_2O bonds with Al_2O_3 in combination with SiO_2 can lead to crystal phases other than the desired aluminoborate bond.

Because of their high fluxing action and their adverse effect upon the formation of the desired lithium aluminoborate phase, the preferred inventive materials will be essentially free from the alkali metal oxides Na_2O and K_2O. By the expression "essentially free from", it is meant that the glass does not contain an amount of a component, for example, Na_2O and/or K_2O, sufficient to alter the chemical and/or physical characteristics of the precursor glass and/or the final glass-ceramic. Preferably, the component will be absent entirely, but that circumstance is not always possible because the batch materials frequently contain the component as an impurity.

MgO appears to augment the action of Li_2O, thereby enabling the level of Li_2O to be maintained at a lower value., while still forming large amounts of the desired crystalline bond phase. It is believed that MgO may form a solid solution within the $2Li_2O{\cdot}3Al_2O_3{\cdot}2B_2O_3$ crystal, perhaps $MgO{\cdot}Li_2O{\cdot}3Al_2O_3{\cdot}2B_2O_3$. MgO also seems to improve the chemical durability of the glass. Concentrations in excess of 12%, however, hazard the development of unwanted refractory crystal phases, such as spinel, in reacting with the particulate alumina.

Laboratory experimentation has indicated that the most desirable physical characteristics will typically be exhibited, both in the precursor glasses and in the crystallized glass-ceramic, in those glass compositions consisting essentially solely of Li_2O, B_2O_3, SiO_2, and, optionally, MgO. Nevertheless, minor additions, generally less than a total of 10%, of compatible inorganic metal oxides such as, for example, Al_2O_3, La_2O_3, CeO_2, MnO, PbO, TiO_2, ZnO, and ZrO_2, can be included to modify the properties demonstrated by the glass and those of the glass-ceramic alumina composite body. Care must be exercised in adding extraneous oxides, however, to avoid the generation of low melting glassy, i. e., uncrystallized, phases in the final product.

The method for preparing the inventive composite bodies comprises the five general steps recited below:

(a) a batch for a thermally crystallizable glass having a composition within the above ranges is melted;
(b) that melt is cooled to a glass body and that body is comminuted to a finely-divided powder;
(c) that powder is blended thoroughly with finely-divided alumina to form a homogeneous mixture of the powders;
(d) that mixture of powders is shaped into a body of a desired configuration; and
(e) that body is heated to a temperature and for a time sufficient to sinter the glass particles together into an integral body while wetting the particles of alumina to a sufficient extent to react with the alumina particles to thereby develop a strong bond with the alumina powders.

As mentioned above, sintering temperatures as low as 750°C can be operable with certain glass compositions. It is well-recognized in the art, however, that sintering, crystallization, and matrix filling reactions take place more rapidly as the temperature is raised. Furthermore, it is also well-recognized in the art that the time necessary for sintering, crystallization, etc., is dependent upon the temperature at which the reactions are carried out. Finally, it is well-recognized in the art that very high reaction temperatures can lead to thermal deformation of the body, extensive reactions that can produce undesirable phases, and even to volatilization of the glass components. Accordingly, a temperature of about 950°C has been deemed to comprise a judicious maximum heat treating temperature. Periods of time ranging about 2-24 hours can be utilized. In general, to assure essentially complete reaction with the alumina particles, a firing period of about eight hours has been deemed to be a practical compromise.

Whereas the three United States patents discussed above, viz., Patent No. 4,861,734, Patent No. 5,112,777, and Patent No. 5,256,603, are believed to constitute the most pertinent prior art, the two patents briefly reviewed below are distantly related to the subject invention.

United States Patent No. 3,006,775 (Chen) discloses and claims the production of glass-ceramic articles consisting essentially, in weight percent, of

Li_2O	4-30	Al_2O_3	3-25
SiO_2	50-80	Fluxing Agent	0-15

wherein B_2O_3 is recited as being a potential fluxing agent. The resulting glass-ceramics contain lithium aluminum silicate crystals and/or lithium silicate crystals, and the use of the materials as a bonding agent for alumina is noted. Nevertheless, it is immediately evident that the level of B_2O_3 is far below the minimum 25% mandated by the Applicants and the crystal phases are unlike those of the Applicants.

United States Patent No. 5,024,974 (Nakamura et al.) discloses and claims glasses exhibiting nonlinear optical effects through the presence of ultrafine particles of CuCl and/or CuBr particles contained therein. The base glasses consist essentially, in mole percent, of

SiO_2	10-70	LiO_2+Na_2O+K_2O	0.1-50
B_2O_3	30-90	CuCl+CuBr	0.01-10
Al_2O_3	0.01-40		

There is no reference to particulate alumina or to the operability of the glass compositions to form bonds with those particles. There is no mention of aluminoborate crystals; the sole crystals described consisted of CuCl and/or CuBr.

Table I reports a number of glass forming compositions, expressed in terms of parts by weight on the oxide basis, illustrating the subject invention. Because the sum of the components totals or very closely approximates 100, for all practical purposes, the tabulated values may be considered to represent weight percent. The actual batch ingredients

can comprise any materials, either the oxides or other compounds, which, when melted together. will be converted into the desired oxide in the proper proportions. For example, Li_2CO_3 and $MgCO_3$ can constitute the sources of Li_2O and MgO, respectively.

The batch materials were compounded, thoroughly blended together to assist in obtaining a homogeneous melt, and charged into platinum crucibles. The crucibles were then introduced into a furnace operating at a temperature of about 1500°C and maintained therewithin for about 1-2 hours.

To reduce the time and energy necessary to comminute the glass to finely-divided particles, the melts were often poured as a fine stream into a bath of tap water. This procedure, termed "drigaging" in the glass art, breaks up the stream of molten glass into small fragments which can then be milled or otherwise powdered to the desired particle size. Another technique commonly used to achieve the same goal includes running a stream of molten glass between metal rollers to form a thin ribbon of glass which was thereafter crushed and milled to the desired particle size.

It must be appreciated that the above description of mixing, melting, and forming procedures reflects laboratory activity only. The inventive glass compositions are capable of being processed utilizing mixing, melting, and forming practices conventionally used in commercial glassmaking. Thus, it is only required that the batch constituents be thoroughly blended together, melted at a sufficiently high temperature for an adequate period of time to secure a homogeneous melt, and subsequently shaped into a glass body.

The glass was reduced to powders having an average particle diameter of about 10µm through ballmilling using Al_2O_3 cylinders as the milling media and methanol as the milling aid. After drying, the powders were thoroughly mixed with Al_2O_3 powders passing a No. 80 U. S. Standard Sieve (117µm) in a vibratory mixer.

TABLE I

	1	2	3	4	5	6
Si_2O	26.2	41.5	38.8	37.0	47.2	51.5
B_2O_3	60.7	48.1	48.3	53.7	41.0	39.9
Li_2O	13.1	10.4	12.9	9.3	11.8	8.6
	7	8	9	10	11	12
Si_2O	46.6	45.5	51.2	50.8	34.4	52.3
B_2O_3	43.3	42.3	39.6	39.3	53.2	40.4
Li_2O	7.0	6.8	6.4	4.2	8.6	4.4
MgO	3.1	--	2.9	5.7	3.9	2.9
MnO	--	5.4	--	--	--	--
	13	14	15	16	17	18
SiO_2	48.4	48.7	46.2	44.0	44.3	42.3
B_2O_3	37.4	37.7	44.7	42.5	42.8	40.1
Li_2O	6.1	8.1	3.9	3.7	5.5	6.5
MgO	8.1	5.5	5.2	9.8	7.4	2.9
Al_2O_3	--	--	--	--	--	7.3
	19	20	21	22	23	24
SiO_2	43.7	44.5	48.4	40.8	43.5	43.2
B_2O_3	33.8	43.0	37.4	47.3	42.0	41.7
Li_2O	5.5	5.6	4.0	5.1	7.2	5.4

Continuation of the Table on the next page

TABLE I (continued)

	1	2	3	4	5	6
	7	8	9	10	11	12
	13	14	15	16	17	18
	19	20	21	22	23	24
MgO	4.9	5.0	5.4	6.8	7.3	9.7
ZnO	--	2.0	--	--	--	--
MnO	--	--	4.8	--	--	--

In order to evaluate porous samples for potential use in bonded abrasives, small (3.5 grams) composite pellets were formed by mixing glass frit [particles passing a No. 325 U.S. Standard Sieve (44 µm)], ceramic particles passing a No. 80 U.S. Standard Sieve (177µm), and small amounts of water at concentrations calculated to yield specific grain-bond proportions. The mixtures were blended by hand, after which cylindrical pellets were dry pressed at 10,000 psi (~703 kg/cm^2) and fired according to selected heat treating schedules. For strength measurements, at least three pellets were prepared and tested at each conditions and the measurements averaged.

After visual examination, the fired composite pellets were subjected to axial compression strength measurements, those values providing a measure of crushing strength. Where compositions and firing schedules yielded particularly high compression strengths, discs thereof having a diameter of 1.5" (~3.8 cm) and weighing 18 grams were prepared and fired in a manner similar to the pellets fired above. Those discs were submitted for modulus of rupture (MOR) testing utilizing a standard piston-on-three-ball technique.

Table II reports the heat treatment schedules applied to the 3.5 gram composite pellets and the 18 gram discs employing an electrically heated furnace. After the final hold temperature, the pellets were cooled at furnace rate; i.e., the electric current to the furnace was cut off and the pellets were allowed to cool to room temperature retained within the furnace.

Table II recites the dwell temperature in °C, along with a qualitative appraisal of the bond crystallinity as estimated via x-ray diffraction analysis of fine powders, a measurement of flexural strength reported as modulus of rupture (MOR), and a measurement of compressive strength, both of those measurements being expressed in terms of MPa and Ksi (thousand psi).

TABLE II

Example	Heat Treatment	Bond Crystallinity	MOR	Compression
1	800	Very High	60.72 MPa; 8.8 Ksi	234.6 MPa; 34 Ksi
2	900	High	70.38 MPa; 10.2 Ksi	255.3 MPa; 37 Ksi
3	850	Very High	--	255.3 MPa; 37 Ksi
4	850	High	--	248.4 MPa;36 Ksi
5	900	Medium	71.07 MPa; 10.3 Ksi	227.7 MPa; 33 Ksi
6	850	Low	84.87 MPa; 12.3 Ksi	255.3 MPa; 37 Ksi
7	900	High	85.56 MPa; 12.4 Ksi	255.3 MPa; 37 Ksi
8	825	Low	86.25 MPa; 12.5 Ksi	282.9 MPa; 41 Ksi
9	900	Medium	85.56 MPa; 12.4 Ksi	269.1 MPa; 39 Ksi
10	850	High	80.04 MPa; 11.6 Ksi	289.8 MPa; 42 Ksi
11	850	High	--	262.2 MPa; 38 Ksi
12	850	Medium	79.35 MPa;11.5 Ksi	276.0 MPa; 40 Ksi
13	900	Medium	84.18 MPa; 12.2 Ksi	269.1 MPa; 39 Ksi
14	900	High	80.04 MPa; 11.6 Ksi	269.1 MPa; 39 Ksi

Continuation of the Table on the next page

TABLE II (continued)

Example	Heat Treatment	Bond Crystallinity	MOR	Compression
15	900	Medium	82.80 MPa; 12.0 Ksi	269.1 MPa; 39 Ksi
16	900	Medium	87.63 MPa; 12.7 Ksi	269.1 MPa; 39 Ksi
17	900	Medium	91.08 MPa; 13.2 Ksi	262.2 MPa; 38 Ksi
18	900	Medium	74.52 MPa; 10.8 Ksi	262.2 MPa; 38 Ksi
19	900	Medium	91.08 MPa; 13.2 Ksi	310.5 MPa; 45 Ksi
20	900	Medium	91.77 MPa; 13.3 Ksi	248.4 MPa; 36 Ksi
21	900	Medium	93.15 MPa; 13.5 Ksi	269.1 MPa; 39 Ksi
22	900	Medium	92.46 MPa; 13.4 Ksi	282.9 MPa; 41 Ksi
23	900	Medium	96.60 MPa; 14.0 Ksi	269.1 MPa; 39 Ksi
24	900	Medium	103.5 MPa; 15.0 Ksi	241.5 MPa; 35 Ksi

The very high mechanical strengths demonstrated by the sintered glass-ceramic-bonded Al_2O_3 particles strongly recommend the inventive thermally crystallizable glasses as bonding media for particulate Al_2O_3 in such applications as grinding wheels and other abrasive products where Al_2O_3 particles comprise the abrasive material.

Whereas the above laboratory work was drawn to forming bulk bodies, it will be appreciated that the inventive materials can be applied as coatings on high temperature refractory ceramics and metals, and as substrates for microelectronic circuitry.

Founded in an overall matrix of physical properties, the glass-ceramic-bonded Al_2O_3 composite comprising Example 17 sintered at 900°C has been deemed to comprise the most preferred embodiment of the invention.

Claims

1. A thermally crystallizable glass consisting essentially, expressed in terms of weight percent on the oxide basis, of

SiO_2	25-55	MgO	0-12
B_2O_3	35-65	Li_2O+MgO	4-16.
Li_2O	2-15		

2. A thermally crystallizable glass according to claim 1 also containing up to 10% total of at least one inorganic metal oxide selected from the group consisting of Al_2O_3, CeO_2, La_2O_3, MnO, PbO, TiO_2, ZnO, and ZrO_2.

3. A thermally crystallizable glass according to claim 1 having a composition which is essentially free from Na_2O and K_2O.

4. A sintered glass-ceramic-bonded ceramic composite body comprising about 70-90% by weight of alumina particulates and about 10-30% by weight of glass-ceramic, said glass-ceramic being crystallized in situ from a glass consisting essentially, expressed in terms of weight percent on the oxide basis, of

SiO_2	25-55	MgO	0-12
B_2O_3	35-65	Li_2O+MgO	4-16.
Li_2O	2-15		

5. A composite body according to claim 4 wherein said glass-ceramic is bonded to said alumina particulates through lithium aluminoborate crystals.

6. A composite body according to claim 4 wherein said thermally crystallizable glass also contains up to 10% total of at least one inorganic metal oxide selected from the group consisting of Al_2O_3, CeO_2, La_2O_3, MnO, PbO, TiO_2, ZnO, and ZrO_2.

7. A composite body according to claim 4 wherein said thermally crystallizable glass has a composition which is essentially free from Na_2O and K_2O.

8. A method for forming a sintered glass-ceramic-bonded ceramic composite body comprising about 70-90% by weight of alumina particulates and about 10-30% by weight of glass-ceramic comprising the steps of

(a) melting a batch for a glass consisting essentially, expressed in terms of weight percent on the oxide basis, of

SiO_2	25-55	MgO	0-12
B_2O_3	35-65	Li_2O+MgO	4-16 ;
Li_2O	2-15		

(b) cooling said melt and simultaneously shaping said melt into a glass body of a desired configuration;
(c) comminuting said glass body into finely-divided powder;
(d) mixing that powder with finely-divided alumina particulates;
(e) shaping said mixture into a body of a desired configuration; and then
(f) heating said body to a temperature and for a period of time sufficient to sinter said glass particles into an integral body while wetting said alumina particulates to a sufficient extent to react with said alumina particulates to thereby develop a strong bond of lithium aluminoborate with said alumina particulates.

9. A method according to claim 8 wherein said glass also contains up to 10% total of at least one inorganic metal oxide selected from the group consisting of Al_2O_3, CeO_2, La_2O_3, MnO, PbO, TiO_2, ZnO, and ZrO_2.

10. A method according to claim 9 wherein said glass is essentially free from Na_2O and K_2O.

11. A method according to claim 8 wherein said body is heated to a temperature between about 750°-950°C.

12. A method according to claim 11 wherein said body is heated to a temperature between about 850°-900°C.

13. A method according to claim 8 wherein said body is heated for a period of time ranging about 2-24 hours.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 40 2387

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DE-A-21 23 251 (HPC PRODUITS CHIMIQUES S.A.) 30 November 1972 * page 2 - page 4, paragraph 1 *	1-3	C03C10/02 C03C14/00
A	EP-A-0 219 807 (NARUMI CHINA CORPORATION) 29 April 1987 * page 3 * * page 6, line 18 - page 8, line 9 *	1-13	
D,A	US-A-5 256 603 (ANDRUS) 26 October 1993 * column 1, line 48 - column 3, line 23 *	1-13	
D,A	US-A-5 112 777 (MACDOWELL) 12 May 1992 * column 2, line 6 - column 3, line 10 *	1-13	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 January 1996	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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